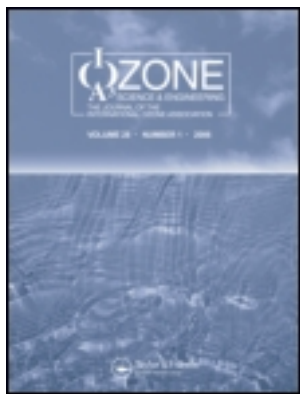


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A Refined Model for Ozone Mass Transfer in a Semibatch Stirred Vessel

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Abstract

The mathematical model proposed by Anselmi et al. (1984) for a semibatch stirred gas-liquid contactor is refined to describe the mass transfer of ozone absorption and decomposition in aqueous solution with the decomposition rate expression of general reaction orders (not necessarily integers). Three system equations are employed to describe the ozone concentrations in the bulk liquid (C_{ALb}), the hold-up gas (C_{AGi}), and the outlet gas in the free volume above the liquid surface (C_{AGe}), respectively. The effect of ozone decomposition on the mass transfer, which is reflected by the enhancement factor (E_r) defined as the ratio of mass absorbed per unit area in time t with chemical reaction (r) to that without chemical reaction or of the purely physical absorption, is considered in the refined model. Furthermore, the refined model also takes into account the variation of E_r with C_{ALb} , which changes with time during the course of gas-liquid contacting. Thus this analysis extends the applicability of the model of Anselmi et al. (1984) and is of special importance for ozone mass transfer in the cases of basic solutions and of low mass transfer coefficients, in which the effect of decomposition on absorption is significant, and in the system with variable liquid phase ozone concentration.

Introduction

Ozone mass transfer is of importance for ozone utilization in a semibatch stirred gas-liquid contactor (Yocum, 1979; Anselmi et al., 1984). For such a semibatch stirred vessel, Anselmi et al. (1984) have developed a three-equation model describing the concentrations of ozone in the bulk liquid (C_{ALb}), the hold-up gas (C_{AGi}), and the free volume above the liquid surface (C_{AGc}). Their model is better than the usual model describing C_{ALb} with the assumption of constant C_{AGi} such as $C_{AGi} = C_{AGi}^0$ (the ozone concentration of the inlet gas). The second order kinetics of ozone decomposition at pH = 5.4 was initially introduced in the system equations, but finally disregarded in obtaining the solution. Thus, their model cannot be applicable for other kinetic expressions of ozone decomposition reported by many investigators (for example, Weiss, 1935; Sheffer and Esterson, 1982; Sotelo et al., 1987; Nadezhdin, 1988; Farooq and Ahmed, 1989; Mehta et al., 1989; Chang et al., 1995). Moreover, in the study of Anselmi et al. (1984), neither the effects of the decomposition reaction (r) on the enhancement factor E , nor the differentiation between the purely physical (k_t^0) and the chemical (k_t) mass transfer coefficients has been provided. The term E_r is defined as the ratio of mass absorbed per unit area in time t with chemical reaction to that of purely physical absorption (Danckwerts, 1970). This lack of information seriously complicates the use of the data for the purposes of: 1) performing mass transfer computations, and 2) computing the mass transfer in combination with different reactions (Bollyky, 1981). Further, the value of E_r varies with C_{ALb} , which changes with time during the course of gas-liquid contacting. All these factors would have to be taken into consideration for properly modeling the ozone mass transfer in a semibatch stirred vessel.

Ozone decomposition reactions have been studied by numerous investigators as can be seen from the tables compiled by Peleg (1976), Teramoto et al. (1981), Gurol and Singer (1982), Sotelo et al. (1987), Nadezhdin (1988), Farooq and Ahmed (1989), and Miyahara and Hirokawa (1994). The overall reaction kinetic orders varied from 0 to 2 for ozone while from 0 to 1 for hydroxide ion (Sheffer and Esterson, 1982; Anselmi et al., 1984; Sotelo et al., 1987; Nadezhdin, 1988; Farooq and Ahmed, 1989). The only agreement reached by these workers is the radical-chain nature of ozone decomposition, which is catalyzed by the hydroxide ion (Sotelo et al., 1987; Nadezhdin, 1988). Among those kinetic schemes based on radical-chain reaction mechanisms, the pioneering work of Weiss (1935) led to a kinetic expression of the form: for pH 2 to 8:

$$-r_{O_3} = k_{1w}[HO^-][O_3] + k_{2w}[HO^-]^{0.5}[O_3]^{1.5} \quad [1]$$

Sotelo et al. (1987) added a second initiation reaction between ozone and water to the scheme of Weiss (1935) to explain an apparent independence of the rate on pH in the acidic region. They suggested that for pH = 2.5 to 9 and temperature = 283 to 313 K,

$$-r_{O_3} = k_{AS}[O_3] + k_{BS}[HO^-]^{0.5}[O_3]^{1.5} \quad [2]$$

Kuo (1982) conducted theoretical studies on the mass transfer during ozone absorption. The decomposition reaction was considered first order with respect to ozone. Mehta et al. (1989) modified the model of Kuo (1982) taking three-halves order with respect to ozone concentration for the decomposition reaction of ozone. The effects of pH value and

temperature were not included in their models. Miyahara and Hirokawa (1994) also suggested a rate expression of ozone decomposition in the form:

$$-r_{O_3} = (k_{1M} + k_{2M}[HO^-]^{0.8})\exp(k_{3M}/T)[O_3]^{1.5} \quad [3]$$

Recently, Chang et al. (1995) gave the following reaction rate expression which is applicable to ozone decomposition of the general form:

$$-r_{O_3} = k_{Am}[O_3]^m + k_{Bn}[O_3]^n \quad [4]$$

In Equation [4], k_{Am} and k_{Bn} represent the acidic and basic decomposition reaction rate constants, respectively. Equation [4] reduces to Equation [1] with $k_{Am} = k_{1M}[HO^-]$, $m = 1$, $k_{Bn} = k_{2M}[HO^-]^{0.8}$, and $n = 1.5$, to Equation [2] with $k_{Am} = k_{As}$, $m = 1$, $k_{Bn} = k_{BS}[HO^-]^{0.5}$, and $n = 1.5$, to Equation [3] with:

$$k_{Am} = k_{1M}\exp(k_{3M}/T), m = 1.5, k_{Bn} = k_{2M}[HO^-]^{0.8}\exp(k_{3M}/T)$$

and $n = 1.5$, and to the rate expressions proposed by other investigators with $k_{Am} = 0$, and $n = 0-2$ (not necessarily an integer). Employing the general reaction rate expression of Equation [4] and applying the film model of gas liquid absorption, Chang et al. (1995) examined the role of the ozone decomposition reaction on E_r and the efficient use of ozone. Further, according to Sotelo et al. (1989 a,b), the kinetic constant of ozone decomposition in solution also is affected by the type of salts, the ionic strength (I), and the hydroxyl radical scavenger concentration (C_{OHS}). For example, at $pH = 7$, and salt type = sodium phosphate (buffered solution), Sotelo et al. (1989a) reported $-r_{O_3}$ as follows:

$$-r_{O_3} = k_{CS}[O_3]^2 = (7.12 \times 10^{10} \exp(-6858/T)I^{1.03}/C_{OHS})[O_3]^2 \quad [5]$$

The units of k_{CS} , T , I , C_{OHS} and $[O_3]$ in Equation [5] are $M^{-1}s^{-1}$, K, M, M and M, respectively. Equation [5] also may be regarded as a special form of Equation [4].

Noting the need for improving and extending the applicability range of the model of Anselmi et al. (1984), this analysis considers the ozone decomposition rate expression of general reaction orders and the enhancement factor, which varies with time during the course of gas-liquid contacting. The refined model presented herein is of special importance for ozone mass transfer in the cases of basic solutions and of low mass transfer coefficients, in which the effect of decomposition on absorption is significant, and in the system with varied liquid phase ozone concentration.

Theoretical Analysis

Consider the mass transfer of ozone absorption and decomposition in a semibatch stirred gas-liquid contactor with the decomposition rate expression of the general form as Equation [4]. Referring to the work of Anselmi et al. (1984) which indicated that, owing to mechanical mixing, bubbles circulate in the reaction vessel randomly and break and coalesce continuously, one may assume that the liquid phase as well as the gas phase are

perfectly mixed as in continuous stirred tank reactors. Thus, the system equations in dimensionless forms describing the concentrations of ozone in the bulk liquid (C_{ALb}), the hold-up gas (C_{AGh}), and the free volume above the liquid surface (C_{AGe}), which are derived from the mass balance and the absorption equilibrium, are as follows:

$$\frac{d\theta_{ALb}}{d\tau} = E_r(\theta_{AH} - \theta_{AL}) - \frac{(m+1)}{2} Sh M_{Am} \theta_{AL}^m - \frac{(n+1)}{2} Sh M_{Bn} \theta_{AL}^n \quad [6]$$

$$\frac{d\theta_{AH}}{d\tau} = \frac{QV_L}{k_L^0 S V_H} (1 - \theta_{AH}) - \frac{V_L}{H_e V_H} E_r (\theta_{AH} - \theta_{AL}) \quad [7]$$

$$\frac{d\theta_{AF}}{d\tau} = \frac{QV_L}{k_L^0 S V_F} (\theta_{AH} - \theta_{AF}) \quad [8]$$

$$\text{at } \tau = 0; \quad \theta_{AL} = 0; \quad \theta_{AH} = 0; \quad \theta_{AF} = 0 \quad [9]$$

The system variables and parameters in dimensionless forms are defined as:

$$\theta_{AL} = \frac{C_{ALb}}{(C_{AGi}^0/He)}, \quad \theta_{AH} = C_{AGi}/C_{AGi}^0; \quad \theta_{AF} = C_{AGe}/C_{AGi}^0 \quad [10]$$

$$M_{Am} = \frac{2D_A k_{Am} (C_{AGi}^0/He)^{m-1}}{(m+1)(k_L^0)^2}$$

$$M_{Bn} = \frac{2D_A k_{Bn} (C_{AGi}^0/He)^{n-1}}{(n+1)(k_L^0)^2}$$

$$\tau = k_L^0 S t / V_L; \quad Sh = k_L^0 V_L / (D_A S)$$

In the previous study on ozone mass transfer in a semibatch stirred vessel, Anselmi et al. (1984) also presented a three-equation model similar to Equations [6]-[8]. However, they employed a second order kinetics of ozone decomposition which may not necessarily be applicable for other kinetics reported by many investigators (for example, Sotelo et al., 1987; Nadezhden, 1988). Furthermore, they did not consider the effect of ozone decomposition on the mass transfer which may be reflected by the enhancement factor E_r . The value of E_r is dependent on the bulk liquid concentration C_{ALb} which varies with time during the course of gas-liquid contacting. The present analysis thus compensates for the lack of the model of Anselmi et al. (1984).

The decomposition reaction may affect the mass transfer rate of ozone. The influence can be reflected by the enhancement factor E_r in Equations [6] and [7]. Therefore, it is necessary to evaluate the enhancement factor E_r in advance for solving Equations [6]-[9].

According to the film model, one may describe the ozone absorption with a decomposition reaction as (Chang et al., 1995) :

$$\frac{d^2\theta_A}{dz^2} = \frac{(m+1)}{2} M_{Am} \theta_{AL}^m + \frac{(n+1)}{2} M_{Bn} \theta_{AL}^n \tag{11}$$

$$\text{at } z = 0; \quad \theta_A = \theta_{AH} = \frac{C_{AGi}/He}{C_{AGi}^0/He} \tag{12}$$

$$z = 1; \quad \theta_A = \theta_{AL} = \frac{C_{ALb}}{C_{AGi}^0/He} \tag{13}$$

with $\theta_A = C_A / (C_{AGi}^0/He)$ and $z = x/x_M = x k_L^0/D_A$. Equations [11]-[13] can be solved for $d\theta_A/dz$:

$$\frac{d\theta_A}{dz} = - \left(M_{Am} \theta_{AL}^{m+1} + M_{Bn} \theta_{AL}^{n+1} + C_{mn} \right)^{0.5} \tag{14}$$

When $z = 0$, $-d\theta_A/dz = (\theta_{AH} - \theta_{AL})E_r$ with $E_r = N_A/N_A$ (ratio of mass flux of A with r to that without r) and Equation [14] holds, one can evaluate the constant of integration, C_{mn} . Thus:

$$C_{mn} = [(\theta_{AH} - \theta_{AL})E_r]^2 - M_{Am} \theta_{AH}^{m+1} - M_{Bn} \theta_{AH}^{n+1} \tag{15}$$

Substituting Equation [15] into [14], one has :

$$\frac{d\theta_A}{dz} = -[M_{Am}(\theta_A^{m+1} - \theta_{AH}^{m+1}) + M_{Bn}(\theta_A^{n+1} - \theta_{AH}^{n+1}) + (\theta_{AH} - \theta_{AL})^2 E_r^2]^{0.5} \quad [16]$$

Integration between $z = 0$, $\theta_A = \theta_{AH}$ and $z = 1$, $\theta_A = \theta_{AL}$ then gives:

$$\int_{\theta_{AL}}^{\theta_{AH}} d\theta_A / [M_{Am}(\theta_A^{m+1} - \theta_{AH}^{m+1}) + M_{Bn}(\theta_A^{n+1} - \theta_{AH}^{n+1}) + (\theta_{AH} - \theta_{AL})^2 E_r^2]^{0.5} = 1 \quad [17]$$

Evaluating the value of E_r from Equation [17] and solving for Equations [6]-[9] by the fourth order Runge-Kutta method, one then can obtain the ozone concentrations at successive absorption times for any specific case.

A number of kinetic expressions of decomposition of ozone in aqueous solutions have been reported by some investigators (for example, Sullivan and Roth, 1980; Sotelo et al., 1987 and 1989a; Mehta et al., 1989; Miyahara and Hirokawa, 1994). In general, the kinetic expressions are dependent on the following operating variables as indicated previously: temperature, pH, type of salt, ionic strength, and hydroxyl radical scavenger concentration. The computations of the present model thus depend on the applicable kinetic expression. There may be suggested different forms of kinetic expressions describing ozone decomposition in aqueous solutions and yielding the simulation results of the model. This, of course, deserves further study in the future. For illustration, the kinetic expression in the form of Equation [2] as reported by Sotelo et al. (1987) is employed. They reported that:

$$k_{AS} = 3.26 \times 10^5 \exp(-4964/T) \quad [18]$$

$$k_{BS} = 5.69 \times 10^{18} \exp(-10130/T) \quad [19]$$

The units of k_{AS} , k_{BS} and T in Equations [18] - [19] are min^{-1} , $\text{L mol}^{-1} \text{min}^{-1}$, and K , respectively. As regards the purely physical mass transfer coefficient k_L^0 and the specific interfacial area a , many measurements and correlations are available. The value of $k_L^0 a$ changes with variables: gas flow rate (Q) or superficial gas velocity (μ_G), stirring rate (N) or power input, and shape factor of vessel (Lopes De Figueiredo et al., 1979; Van't Riet, 1979; Yocum, 1980; Anselmi et al., 1984; Kawase and Moo-Young, 1988). Sherwood et al. (1975) reported k_L^0 with a range of 0.001 to 0.1 cm s^{-1} . Other investigators gave the following k_L^0 values: $0.00826 \text{ cm s}^{-1}$ (Sotelo et al., 1989a), 0.0142 cm s^{-1} (Bollyky, 1981), 0.025 cm s^{-1} (Roustan et al., 1981), and 0.04 cm s^{-1} (Reith, 1968).

In order to compare the predicted results to the experimental data of Sotelo et al. (1989a), a k_L^0 of $0.00826 \text{ cm s}^{-1}$ is chosen for simulation. Furthermore, in order to examine the case of very low k_L^0 value, a k_L^0 of 0.001 cm s^{-1} also is used. Calderbank (1958) observed the interfacial area a in the range of 0.8 to 4 cm^1 (with $N = 10.5$ to 25 rps) for water in an agitated absorber with μ_G of 1.50 cm s^{-1} and tank diameter (d_T) of 19.1 cm . At $N = 12 \text{ rps}$, the value of a is about 1 cm^1 . Reith (1968) obtained the values of a in the range 0.8 to 30 cm^1 with $\mu_G = 4.7 \text{ cm s}^{-1}$, $N^3 d_T^2 = 0.2 \times 10^4$ to $150 \times 10^4 \text{ cm}^2 \text{ s}^{-3}$ ($d_I = \text{impeller diameter}$)

and d_T 19.1 to 120 cm. For $d_r = 44.8$ cm, $a = 1.2$ cm⁻¹ at $N^3 d_r^2 = 0.7 \times 10^4$ cm² s⁻³. In the study of Sotelo et al. (1989a), an experimental system with the value of a of 0.157 cm⁻¹ was used. For illustration, the value of a of 1 cm⁻¹ is employed for model simulations. The values of some physical properties of an O₃/H₂O system at 298 K are: $D_A = 2 \times 10^{-5}$ cm² s⁻¹ (Sherwood et al., 1975; Perry and Chilton, 1984), $C_{AGi}^0 = 0.0015$ mol L⁻¹ (Anselmi et al., 1984). The Henry's law constant (He) is dependent on temperature and ionic strength as indicated by Danckwerts (1970). The values of He of ozone-water systems reported by many investigators are:

at T = 298 K:

He [kPa mol fr⁻¹] x 10⁻⁵ = 6.57 (Kuo et al., 1977), 6.41 (Roth and Sullivan, 1981), 5.24 (Kosak-Channing and Helz, 1983), 4.6 (Perry and Chilton, 1984), 4.7 (Ouederni, 1987), 6.57 (Langlais et al., 1991), 5.7 (Miyahara and Hirokawa, 1994),

or 1/He [M(gas)/M(solution)] = 0.209, 0.214, 0.261, 0.299, 0.291, 0.209, 0.245,

at T = 296 K:

He [kPa mol fr⁻¹] x 10⁻⁵ = 6.2 (Caprio et al., 1982; Anselmi et al., 1984),

or 1/He [M(gas)/M(solution)] = 0.223,

at T = 293 K:

He [kPa mol fr⁻¹] x 10⁻⁵ = 3.81 (Bollyky, 1981), 5.67 (Sotelo et al., 1989a),

or 1/He [M(gas)/M(solution)] = 0.335, 0.242.

The differences of the properties of solutions used by these investigators may cause the above differences of the values of He, reflecting the complicated nature of ozone-water systems. For simulation illustration, 1/He [M(gas)/M(solution)] of 0.223 (Caprio et al., 1982; Anselmi et al., 1984) is employed. The values of V_L , V_H , V_F and Q are chosen by referring to the work of Anselmi et al. (1984).

It is worth noting that the usual model describing C_{ALb} in a stirred vessel assuming constant C_{AGi} such as $C_{AGi} = C_{AGi}^0$ is as follows.

$$\frac{d\theta_{AL}}{d\tau} = E_r(1 - \theta_{AL}) - \frac{m+1}{2} ShM_{Am} \theta_{AL}^m - \frac{n+1}{2} ShM_{Bn} \theta_{AL}^n \quad [20]$$

$$at \tau = 0, \quad \theta_{AL} = 0 \quad [21]$$

The corresponding film-model equation for evaluating E_r is similar to Equation [17] with $\theta_{AH} = 1$.

Results and Discussion

Figures 1, 2 and 3 compare the ozone concentrations in the bulk liquid in a semibatch stirred vessel employing three-equation models of different types. The model of this analysis with Equations [6]-[9] includes the variable E_r and the generalized ozone decomposition reaction rate expression which is dependent on the pH value. The model equations of Anselmi et al. (1984) are similar to Equations [6]-[9] with $E_r = 1$ and neglecting the ozone decomposition reaction terms. Thus, the model of this analysis is applicable for the solutions of any pH value, while that of Anselmi et al. is useful only for the solutions of very low pH value as clearly indicated in Figures 1, 2 and 3. In fact, the model of Anselmi et al. (1984) was not valid for the cases of basic solutions.

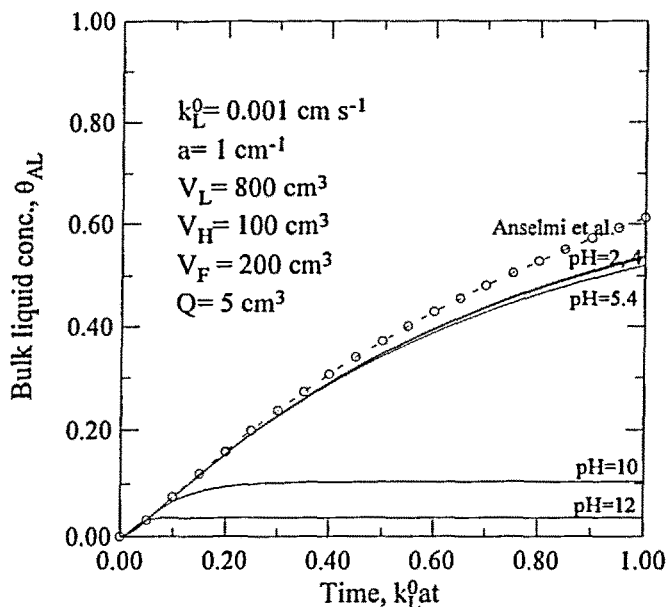


Figure 1. Comparison of θ_{AL} vs time employing three-equation models. "—": this analysis (including E_r and reaction terms); "o": theoretical results using model of Anselmi et al. (1984); "-----": this analysis with $E_r = 1$ and neglecting reaction terms. $a = 1 \text{ cm}^{-1}$, $V_L = 800 \text{ cm}^3$, $V_H = 100 \text{ cm}^3$, $V_F = 200 \text{ cm}^3$, $Q = 5 \text{ cm}^3 \text{ s}^{-1}$, $k_L^0 = 0.001 \text{ cm s}^{-1}$.

The numerical results for the special case of this analysis with $E_r = 1$ and without reaction terms are in good agreement with the theoretical results of Anselmi et al. Figure 4 compares the predicted values of the proposed model to the experimental data of Sotelo et al. (1989a), also indicating good agreement. All these support the validity of the numerical methods and the model employed herein. However, it is noted that the value of the equilibrium liquid concentration obtained from the intercept of the plot of $k_{CS}[O_3]^2 + d[O_3]/dt$ vs $[O_3]$ in Figure 10 of Sotelo et al. (1989a) is about $2.5 \times 10^{-4} \text{ M}$, while that calculated from Henry's law with $P_{O_3} = 2 \text{ kPa}$ is about $1.96 \times 10^{-4} \text{ M}$. The applicable conditions of Sotelo et al. (1989a) in Figure 4 of the present study are: $T = 293 \text{ K}$, $\text{pH} =$

7, $P_{O_3} = 2 \text{ kPa}$, $Q = 60 \text{ L hr}^{-1}$, $N = 100 \text{ rpm}$, salt type = sodium phosphate (buffered solution), $I = 0.15 \text{ M}$, $C_{OHS} = 0.37 \text{ M}$, $He = 5.67 \times 10^5 \text{ kPa mol fr}^{-1} = 4.33 \text{ M(gas)/M(solution)}$, $k_{CS} [\text{M}^{-1}\text{s}^{-1}] = 7.12 \times 10^{10} \exp(-6858/T) I^{1.03}/C_{OHS}$, $-r_{O_3} = k_{CS}[O_3]^2 = 1.864 [O_3]^2$, $k_L^0 = 0.00826 \text{ cm s}^{-1}$, $k_L^0 a = 0.0013 \text{ s}^{-1}$. The gas holdup ϵ_G is estimated to be 0.008 by using the correlation equation for water in the stirred vessel with a four-blade paddle, $\epsilon_G = 0.316 (QN/\sigma)^{0.5}$ (Hassan and Robinson, 1977). The units of Q , N and σ in the ϵ_G equation are m^3s^{-1} , rps and Nm^{-1} , respectively.

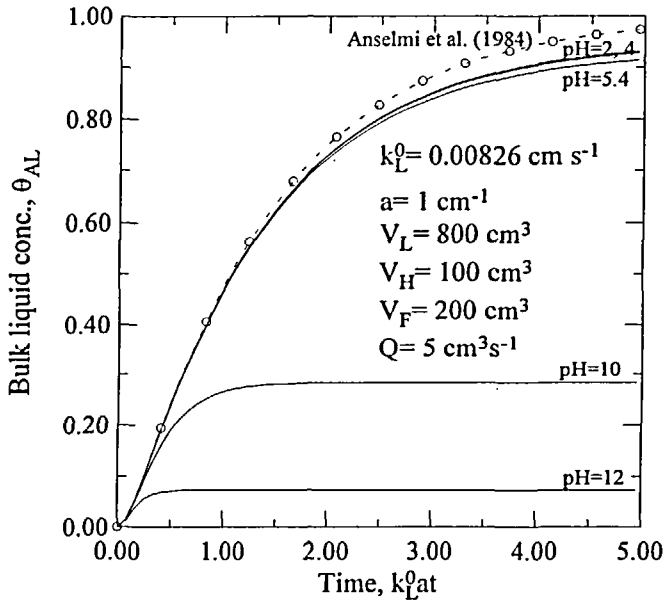


Figure 2. Comparison of θ_{AL} vs time employing three=equation models. $k_L^0 = 0.00826 \text{ cm s}^{-1}$. Notation and other parameter values are the same as in Figure 1.

Also from Figures 1, 2 and 3, it can be observed that when the semi-batch reactor system approaches its steady state, a higher pH value results in a lower steady-state ozone concentration in bulk solution. This is because the rate of ozone decomposition increases with pH value. It is noted that the steady-state concentration does not correspond to the equilibrium, similar to the phenomena described by Sotelo et al. (1989a) and Miyahara and Hirokawa (1994). In fact, the steady-state concentration of C_{ALb} is related to the equilibrium concentration of C_{AGi}/He according to the steady-state form of Equation [6] with $V_L d\theta_{AL}/d\tau = 0$.

In dealing with the purely physical mass transfer of gas in a semibatch stirred vessel, one usually assumes a constant C_{AGi} such as $C_{AGi} = C_{AGi}^0$ (Adams et al., 1981). A model similar to Equation [20] with $E_r = I$ and without reaction terms has been applied to describe the bulk liquid concentration in the purely physical mass transfer system. To test the validity of such model assuming $C_{AGi} = C_{AGi}^0$ to the chemical mass transfer of ozone ($E_r \neq 1$), the results of the model with Equation [20] are obtained and compared with those of the

three-equation model of this analysis. The comparison results of the ozone concentrations in the bulk liquid (θ_{AL}) are presented in Figures 5 and 6. For the conditions specified in the figures, at dimensionless time of 1, the relative deviations of θ_{AL} employing the model with $C_{AGI} = C_{AGI}^0$ from those employing the three-equation model of this analysis are about 6.4% and 18.4% for $k_L^0 = 0.001$ and $0.00826 \text{ cm s}^{-1}$, respectively.

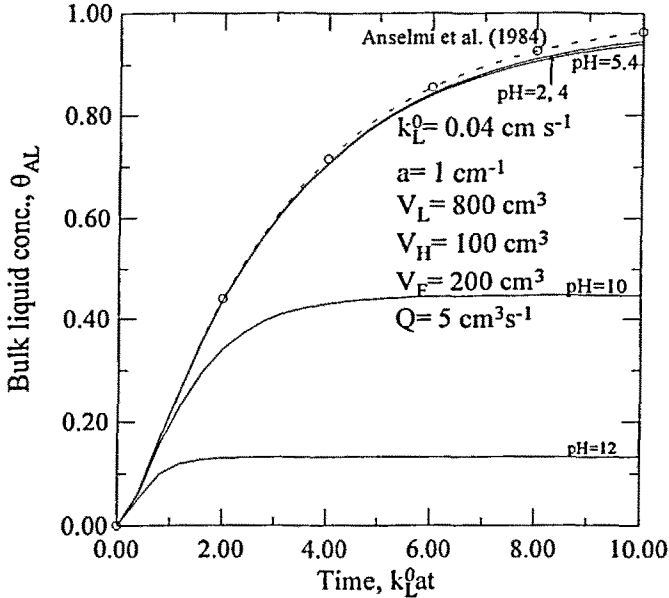


Figure 3. Comparison of θ_{AL} vs time employing three-equation models. $k_L^0 = 0.04 \text{ cm s}^{-1}$. Notation and other parameter values are the same as in Figure 1.

The comparison results of the corresponding E_r illustrated in Figures 7 and 8 also reveal the deviations of the two models. All these again clearly indicate the significant improvements of the present model over the usual model assuming $C_{AGI} = C_{AGI}^0$. Further, Figures 9 and 10 illustrate the difference between the concentrations of the hold-up gas (θ_{AH}) and the outlet gas in the free volume above the liquid surface (θ_{AF}). In practice, one usually measures the concentrations of θ_{AF} and θ_{AH} instead of θ_{AH} and θ_{AL} . A proper model should allow one to relate θ_{AF} to θ_{AH} and then to θ_{AL} . Thus, the refined three-equation model of this analysis is more rigorous and appropriate to describe the ozone mass transfer in a semibatch stirred vessel.

Concluding Remarks

1. The ozone decomposition reaction rates (r_{O_3}) and the enhancement factor (E_r) should be included in the system equations describing the ozone mass transfer in a semibatch stirred gas-liquid contactor.

2. The refined three-equation model with r_{O_3} and variable E_r and considering the concentrations of ozone in the bulk liquid, the hold-up gas and the free volume above the liquid surface is more rigorous and adequate to describe the system performance.

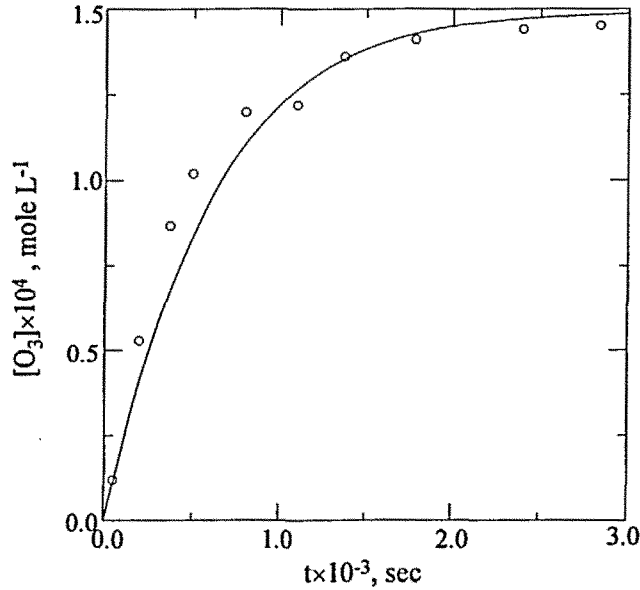


Figure 4. Comparison of ozone concentration by model prediction "—" with experimental data "o" of Sotelo et al. (1989a). $T = 293$ K, $pH = 7$, $P_{O_3} = 2$ kPa, $Q = L$ h $^{-1}$, $N = 100$ rpm, $I = 0.15$ M, salt type = sodium phosphate (buffered solution), $C_{OHS} = 0.37$ M, $k_L^0 = 0.00826$ cm s $^{-1}$, $a = 0.157$ cm $^{-1}$.

Nomenclature

- A ozone species
- a interfacial area per unit volume of liquid, S/V_L
- C_A concentration of A in film according to film model
- C_{AGe} gas concentration of A in free volume
- C_{AGi} concentration of A in hold up gas
- C_{AGi}^0 concentration of A of inlet gas
- C_{ALb} concentration of A in bulk liquid
- C_{AL}^0 equilibrium liquid concentration with $C_{AGi}^0 = C_{AGi}^0/He$
- C_{AL}^* equilibrium liquid concentration with $C_{AGi} = C_{AGi}/He$
- C_{mn} constant of integration given in Equation [15]

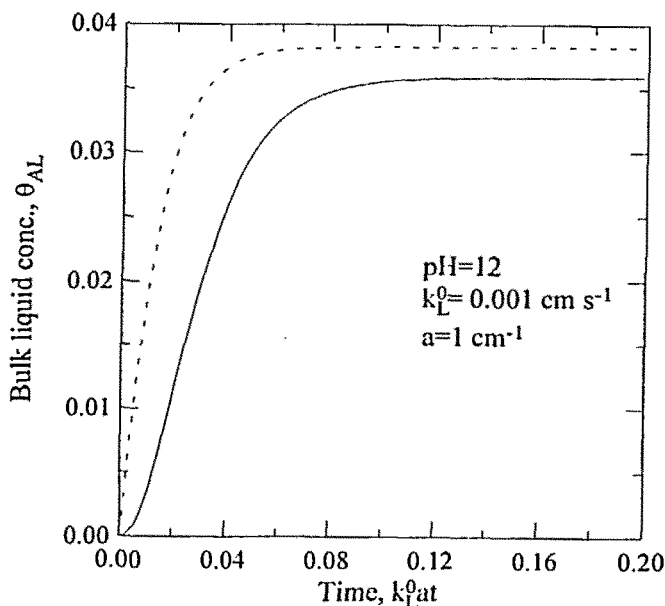


Figure 5. θ_{AL} vs time employing different simulation models. "—" : three-equation simulation of this analysis; "----" : simulation of model assuming $C_{AGi} = C_{AGi}^0$; $a = 1 \text{ cm}^{-1}$, $V_L = 800 \text{ cm}^3$, $V_H = 100 \text{ cm}^3$, $V_F = 200 \text{ cm}^3$, $Q = 5 \text{ cm}^3 \text{ s}^{-1}$, $\text{pH} = 12$, $k_L^0 = 0.001 \text{ cm s}^{-1}$.

C_{OHS}	hydroxyl radical scavenger concentration
d_T	tank diameter
D_A	diffusivity of A
E_r	enhancement factor with effect of self-decomposition reaction (or reaction), N_A/N_A
He	Henry's law constant $C_{AL}^* = C_{AGi}/\text{He}$
I	ionic strength of solution
k_{Am} , k_{Bn}	acidic and basic decomposition rate constants in kinetic expression of Chang et al. (1995) defined in Equation [4]
k_{AS} , k_{BS}	acidic and basic decomposition rate constants in kinetic expression of Sotelo et al. (1987) defined in Equation [2]
k_{CS}	decomposition rate constant in kinetic expression of Sotelo et al. (1989a) defined in Equation [5]
k_L^0	purely physical liquid-phase mass transfer coefficient
k_L	liquid-phase mass transfer coefficient for a specific case, e.g., with chemical reaction
m, n	acidic and basic decomposition reaction orders with respect to O_3 in kinetic expression
M_{Am}	dimensionless acidic decomposition reaction rate parameter, $[2D_A k_{Am} (C_{AGi}^0/\text{He})^{m-1}/(m+1)]/(k_L^0)^2$

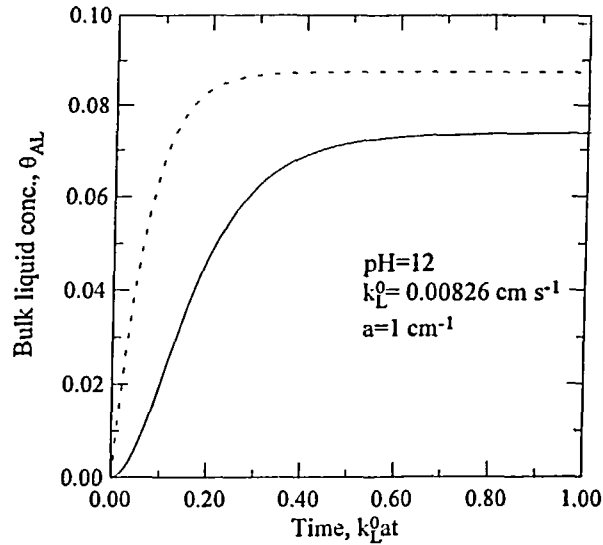


Figure 6. θ_{AL} vs time employing different simulation models. $k_L^0 = 0.00826 \text{ cm s}^{-1}$. Notation and other parameter values are the same as in Figure 5.

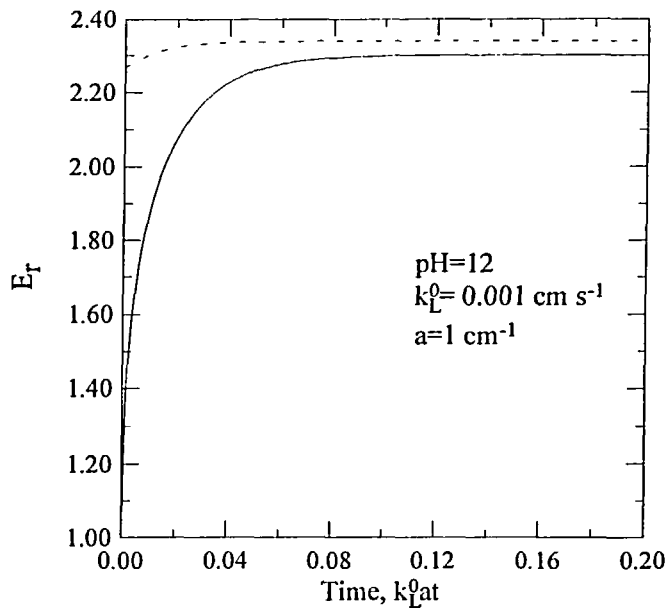


Figure 7. E_r vs time employing different simulation models. "—" : three-equation simulation of this analysis; "-----" : simulation of model assuming $C_{AGi} = C_{AGi}^0$; $a = 1 \text{ cm}^{-1}$, $V_L = 800 \text{ cm}^3$, $V_H = 100 \text{ cm}^3$, $V_F = 200 \text{ cm}^3$, $Q = 5 \text{ cm}^3 \text{ s}^{-1}$, $\text{pH} = 12$, $k_L^0 = 0.001 \text{ cm s}^{-1}$.

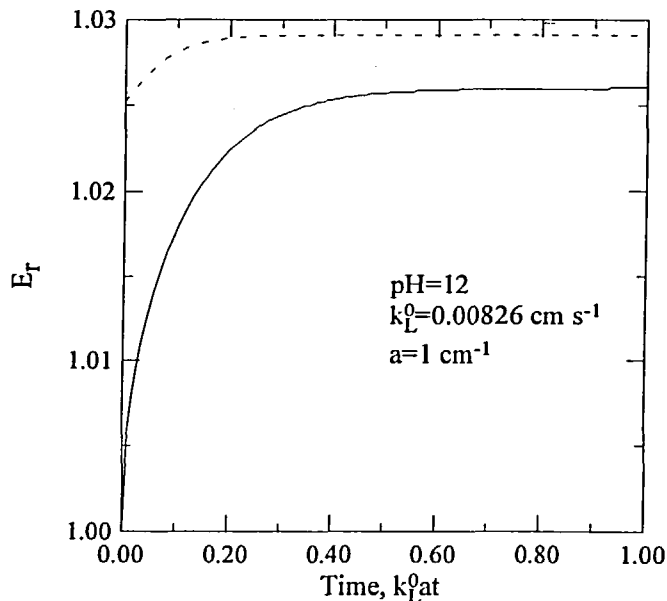


Figure 8. E_T vs time employing different simulation models. $k_L^0 = 0.00826 \text{ cm s}^{-1}$. Notation and other parameter values are the same as in Figure 7.

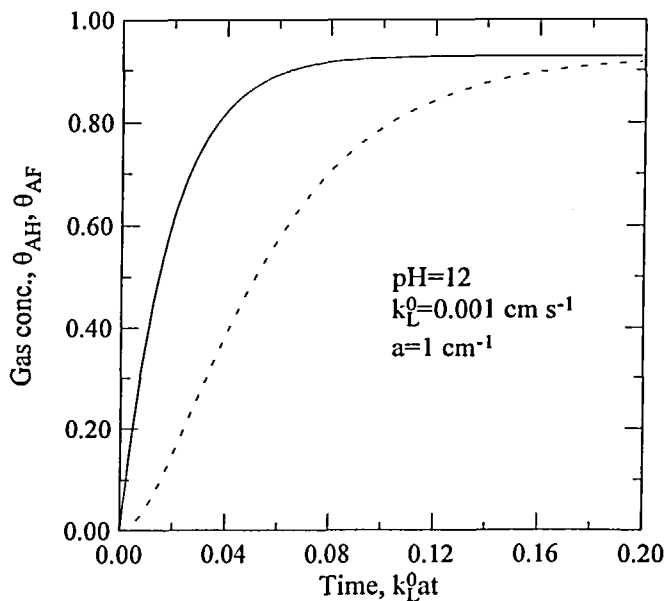


Figure 9. θ_{AH} , θ_{AF} vs time. "—": θ_{AH} , "----": θ_{AF} (three-equation simulation of this analysis). $a = 1 \text{ cm}^{-1}$, $V_L = 800 \text{ cm}^3$, $V_H = 100 \text{ cm}^3$, $V_F = 200 \text{ cm}^3$, $Q = 5 \text{ cm}^3 \text{ s}^{-1}$, $\text{pH} = 12$, $k_L^0 = 0.001 \text{ cm s}^{-1}$.

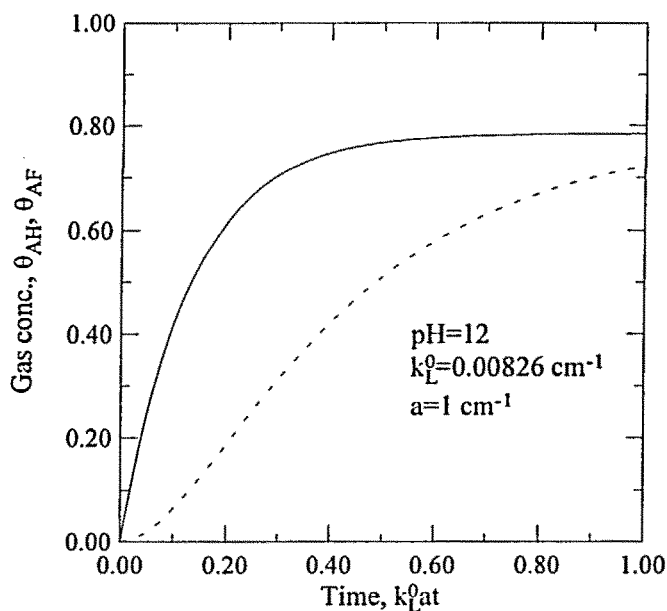


Figure 10. θ_{AH} , θ_{AF} vs time. $k_L^0 = 0.00826 \text{ cm s}^{-1}$. Notation and other parameter values are the same as in Figure 9.

M_{Bn}	dimensionless basic decomposition reaction rate parameter, $[2D_A k_{Bn} (C_{AGi}^0/He)^{n-1}/(n+1)]/(k_L^0)^2$
N	agitation speed
N_A	mass flux of purely physical mass transfer, $k_L^0 [(C_{AGi}^0/He) - C_{ALb}]$ according to film model
N_{Ar}	N_A with self-decomposition reaction (r), $-D_A d_{CA}/dx$
P_{O_3}	ozone partial pressure
Q	gas flow rate
r	reaction rate
S	mass transfer area
Sh	Sherwood number, $k_L^0 V_L (D_A S)$
t	time
T	temperature
U_G	superficial gas velocity
V_F	free volume above liquid surface
V_H	gas hold up volume
V_L	liquid volume
x	distance from gas-liquid interface into liquid film
X_M	thickness of liquid film representing liquid-phase mass transfer resistance, D_A/k_L^0
z	dimensionless x , x/x_M
ϵ_G	dimensionless gas hold up, $V_H/(V_L + V_H)$
θ_A	dimensionless C_A , $C_A/(C_{AGi}^0/He)$

θ_{AF}	dimensionless C_{AGe} , C_{AGe}/C_{AGi}^0
θ_{AH}	dimensionless C_{AGi} , C_{AGi}/C_{AGi}^0
θ_{AL}	dimensionless C_{AL} , $C_{AL}/(C_{AGi}^0/He)$
σ	surface tension
τ	dimensionless time, $k_L^0 S t / V_L$

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Key Words

Ozone; Aqueous Ozone; Decomposition of Aqueous Ozone; Mass Transfer, Semibatch Vessel;

Résumé

Le modèle mathématique proposé par Anselmi et autres (OS&E 6:17, 1984) pour un réacteur gaz-liquide agité en semi-batch est affiné pour décrire le transfert de masse de l'ozone absorbé et sa décomposition dans la solution aqueuse incluant l'ordre des réactions de décomposition de la réaction générale. Un système de trois équations est utilisé pour décrire la concentration en ozone dans le liquide (C_{ALB}), dans les bulles de gaz (C_{AGL}) et le gaz s'échappant au dessus du liquide (C_{AGE}). L'effet de la décomposition de l'ozone sur le transfert de masse, qui est exprimé par le facteur d'amélioration (E_r) est pris en compte dans ce modèle. Le facteur d'amélioration est défini comme étant le rapport de la masse absorbée par unité de surface dans un temps t lorsqu'il y a réaction chimique (r) à la masse absorbée sans réaction chimique (absorption purement physique). En outre, le modèle amélioré prend aussi en compte les variations de E_r en fonction de C_{ALB} , qui change dans le temps au cours de contact gaz-liquide. Cette étude permet d'étendre l'applicabilité du modèle d'Anselmi et autres (1984); elle est d'importance particulière pour le transfert de masse dans le cas de solutions basiques et de faibles coefficients de transfert, pour lesquels l'effet de la décomposition sur l'absorption est significatif, et dans le cas des systèmes avec concentration variable de l'ozone.

Zusammenfassung

Das von Anselmi (OS&E 6:17, 1984) vorgeschlagene mathematische Modell für einen gerührten Gas/Flüssig-Batchreaktor wird verbessert, um den Stoffübergang für die Ozonabsorption und die Ozonzersetzung in wässriger Lösung mit einem Term allgemeiner Reaktionsordnung für die Zersetzung zu beschreiben. Drei Systemgleichungen werden benutzt, um die Ozonkonzentrationen in der Flüssigkeit (C_{ALB}), dem Gas (C_{AGL}) und dem Abgas im Volumen über der Flüssigkeit (C_{AGE}) zu beschreiben. Der Einfluß der Ozonzersetzung auf den Stoffübergang, der ausgedrückt wird durch einen Verstärkungsfaktor (E_r), definiert als das Verhältnis des absorbierten Stoffes, pro Flächeneinheit in der Zeit t mit der chemischen Reaktion (r), zu dem ohne chemische Reaktion bzw auf die rein physikalische Absorption bezogen, wird als das verbesserte Modell bezeichnet. Darüber hinaus berücksichtigt das verbesserte Modell die Schwankung von E_r mit C_{ALB} , die sich mit der Zeit während des Gas/Flüssig-Austausches ändert. So ermöglicht diese Analyse eine erweiterte Anwendung des Modells von Anselmi und ist besonders wichtig für den Ozonübergang bei Lösungen und niedrigen Stoffübergangskoeffizienten, bei denen der Effekt der Ozonzersetzung auf die Absorption besonders groß ist und in Systemen mit schwankenden Ozonkonzentrationen in der Flüssigphase.